

The Influence of Gaseous Pollutants on Silver Artifacts Tarnishing

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Abstract

The present work investigated the effect of the common gaseous pollutants on silver artifacts corrosion. The study will be carried out on manufactured coupons of silver alloy (91 silver, 9 copper) which have chemical composition similar to ancient Egyptian silver artifacts. These coupons will be exposed to gaseous pollutants of each individual gas; such as Sulfur dioxide, Nitrogen dioxide, Carbon dioxide, Hydrogen sulfide and Chlorine. The exposure period will be four weeks in a climate chamber with gas concentration 10 PPM. After the test Examinations by SEM and PM were used to evaluate the effect of each gas and description the morphology of the corrosion layers. The results revealed that all gases reacted with the surface except carbon dioxide. The formed tarnishing layers varied in coverage and density rate. Corrosion products are analyzed by XRD and the results revealed Ag_2S , $AgCl$, Ag_2SO_4 and Ag_2O as corrosion products.

Keywords

Silver, Artifacts, Atmospheric Corrosion, Gaseous Pollutants

1. Introduction

Archaeological silver and its alloys have relatively high resistance to corrosion products in the atmospheric environment compared to copper and iron objects. But in the presence of humidity and gaseous pollutants—special Sulphur containing pollutants—Silver is susceptible to the tarnishing and corrosion products will be formed. Many corrosion products such as Ag_2S , Ag_2SO_4 , $AgCl$, have been identified on silver objects either in museum environment (displayed in cabinets and stored in depositories) or excavated from the burial environment. Silver objects corrosion in the atmospheric environmental attributed to the water layers on the surface which provide the reaction of the gaseous pollutants such as chloride anions, sulphates, carbonates

and Sulphides with metallic surface and lead to the metal dissolution [1].

Among the family of ancient metals, the fewest studies on the laboratory and field exposure of the gaseous pollutants were presented to silver. Previous lab exposure tests often focused on silver tarnish due to Sulphur containing pollutants [2]-[7]. These studies have been agreed in their results which can be summarized in the formation of silver tarnish as black layer consisting of Ag_2S as major corrosion product and Ag_2SO_4 in a negligible quantity. Few lab exposure studies have been presented to impact other gaseous pollutants such as Cl , NO_2 , and CO_2 , but the results were different and varied. The differences were as follow.

Results of Previous studies indicated that nitrogen dioxide is not considered a corrosion factor of silver because silver does not react with it, but it only acts as an accelerated factor of silver tarnish with other gases [8] [9] [10] [11] [12] even though Previous study found silver nitrate Ag_2NO_3 as corrosion products on exposed silver to 1.2 ppm NO_2 for 40 hours [2].

Also Ag_2SO_4 as corrosion product was observed on silver coupons in field exposure [13] although the studies indicated that Silver sulfate (Ag_2SO_4) forms only in artificially high levels of sulfur dioxide [14] [15].

Silver is sensitive to chloride (Cl^-) and silver chloride will be formed as a result of the reaction [10] [11] [12] [15] [16] [17]. Also this does not agree with results revealed that silver chloride compound was not identified on surface film of silver coupons after the exposure in an ASTM B117 salt spray chamber [18] and this compatibility with previous studies mentioned that silver does not react directly with chlorine gas and the presence of silver chloride as corrosion product due to burial in a chloride rich environment [19] [20].

The laboratory-exposure studies of the effect of CO_2 gas on silver are very few, although Ag_2CO_3 is distinguished as corrosion product of silver as result of the reaction with CO_2 and although CO_2 is abundant in the ambient environment of silver artifacts. So very little is known about the formation mechanism of Ag_2CO_3 Such as it is expected only in strong alkaline solutions [21]. Ag_2CO_3 product corrosion has not been detected as corrosion product on the silver artifacts. Also Ag_2CO_3 was identified in a recent study of field-exposure study on the silver coupons exposed to various outdoor environments and the product was detected only in one site which distinguished above the temperature inversion layer [1].

Therefore, in this study, the effects of gases (NO_2 , Cl , CO_2) on silver will be presented as a laboratory exposure and the results will be compared with previous studies. Also they did not take sufficient laboratory studies although they were common gaseous pollutants in outdoor and indoor atmospheric environment, also hydrogen sulfide and sulfur dioxide were chosen as main gases in silver tarnish and lead to silver sulfide which was often observed as corrosion product of silver.

2. Experimental Procedures

2.1. Coupons Preparation

Silver coupons should be similar for archaeological silver of ancient Egypt civili-

zation, different concentrations were found in Ancient Egyptian Silver, elemental analysis of a number of Egyptian silver artefacts showed that the concentration of silver in 10 objects between 83 to 90%, and between 90 to 95% of 19 other objects [22] [23]. Also analyses of Babylonian coins from silver copper alloy were about 87% - 90% purity [21]. So that a composition of coupons was Ag 89.4% and Cu 10.5% .This concentration was not artificial available and was manufactured by alloying a mixture of silver (pieces from the pure silver) with pure copper pieces. The coupons were made by direct addition of silver and copper in a crucible **Figure 1** [24]. The dimensions were (3 cm × 5 cm × 0.08 cm) **Figure 2**. XRF analysis used to determine the Composition.

Thin thickness of coupons about 8 m will be suitable and similar to silver artefacts thickness. most the silver artefacts were manufactured to thin sheets such as thin sheets for royal garments, hollow statues, jewellery items, funeral items, Household items of everyday life such as, spoons, jugs, cups, vessels, pots, covered wooden object, bowls and Other usages. Successive processes of hammering and ductility with the annealing on alloy rod to obtain thin thickness about 0.8 mm. Five new coupons were used for each gas test; a hole was drilled in each sample for suspension in the chamber middle [21].

2.2. Design and Preparation of Climate Chamber Test

Climate chamber was designed according to ASTM [25]. It is made of 1000 cm



Figure 1. Manufacturing to silver coupons: (a) Pure silver pieces; (b) Shape of resulting rod after casting; (c) Cutting coupons after ductility and hammering processes.

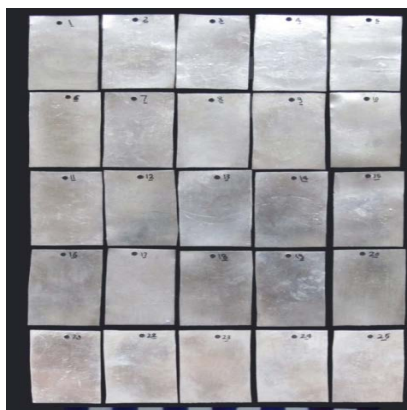


Figure 2. Silver alloy coupons before the exposure.

diameter Perspex cylinder. The humidity was controlled gradually by the cup of saturated salt solution inside the chamber, the approximately 85% RH was obtained by a saturated solution of potassium chloride [26] and the chamber was only opened to remove coupons. Heating of the air inside the chamber is done by a cartridge heater, the air inside the chamber is continuously mixed by a fan, which was suspended from the ceiling of the chamber, the temperature and relative humidity inside the chamber are continuously measured by a data logger device [27] [28]. A few studies were presented on the silver deterioration tests inside climate chamber, these studies used two types of the deterioration factors: high relative humidity [10] [29] and gaseous pollutants in presence relative humidity [2] [25] [29]. Most studies of silver deterioration were used corrosive solutions as deterioration factors, such as BaS 5 g/l solution for 24 Hours [18] and Na₂S were used as the tarnishing solution [30] [31]. Acetic acid solutions were used as simulation of emissions vapors in wooden cabinets and CuCl₂ 50 g/l for 20 min, and NaCl [29] were used of AgCl silver patina [19].

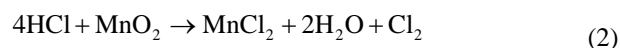
2.3. The Test Gases

The gases for the test were as follows: Sulfur dioxide SO₂, Nitrogen dioxide NO₂, Carbon dioxide CO₂, Chlorine gas Cl and Hydrogen Sulphide H₂S. The gas is mixed with the present air in inside chamber. Those types were the most influence in deterioration of silver artefacts.

2.4. Test Procedures

Each five coupons were exposed to humidified air containing concentration 10 ppm of one gas only. Accelerated conditions parameters were as shown in **Table 1**. The values of conditions parameters were chosen after survey of 29 previous studies which included lab exposure of ancient metals family (copper, bronze, silver, steel and lead) as shown in **Table 2**. Their most experiments were performed at room temperature (22°C - 25°C), and relative humidity between 80 - 90. The other two factors such as the gases concentration and the exposure period differed from study to another.

Cylinders 99.9% concentration were used to obtain of CO₂, SO₂ and NO₂ gases, The gas flowed from cylinder into the exposure chamber after the calculation of flow and time of the required concentration. H₂S and Cl⁻ were prepared in lab, H₂S prepared by the reaction of hydrochloric acid diluted with ferrous sulfide (Equation (1)) [51] and Cl⁻ prepared by the interaction of concentrated Cl⁻ with manganese dioxide (Equation (2)) [52]. According to the law of Avogadro and Lussac can be calculated Volume which the required concentration of H₂S and Cl⁻ inside the chamber is occupied. Where Molecular weight (one mole) of any gas under standard conditions is occupied 22,400 ml (The molar volume, Equation (3)) [53], and by the calculated of molecular weight to H₂S Equation (4) which occupied 22,400 ml can be calculated volume of the required concentration of H₂S Equation (5).



$$1 \text{ mole of a gas at STP} = 22.4 \text{ liters of a gas} \quad (3)$$

$$2 \times 1 + 32 = 34 \text{ g} = 22400 \text{ ml} \quad (4)$$

$$10 \text{ ppm} \left(19 \text{ mg/m}^3 \right) = X \quad (5)$$

Gas syringe was used to get the required volume and injected it into inside chamber **Figure 3**, the fan was used for mixing gases and its distribution inside the chamber.

Table 1. Conditions and procedures of the test.

Period	T	RH	Concentration
8 weeks	25°C	85%	10 ppm

Table 2. Summarizes lap exposure conditions to gaseous pollutants with ancient metals in the previous studies.

Ref.	Gas	Time	Concentration	C	RH	Coupons
[32]	OCS, H ₂ S, SO ₂	5 week	2.5 - 0.26 ppm 2.66 - 3.64 ppm	22	50	Silver
[33]	SO ₂ , NO ₂	30 hours	10 - 22 ppm, 1.8 ppm	25	80% - 90%	Tin
[34]	H ₂ S	22 - 77 days	50 ppb, 2 ppm	30, 80	40%	Copper
[35]	SO ₂ +NO ₂		75 SO ₂ + 120 ppb NO ₂			Copper
[36]	Acetic and formic acid vapors	One, two and four weeks	formic acid 160 ppb, acetic acid 170 ppb, CO ₂ 350 ppm	22	95%	Lead
[37]	H ₂ S, NO ₂ , Cl ₂	4, 10 days	10, 200, 10 ppb	30	70%	Copper
[38]	Mixture of NO ₂ , SO ₂ , O ₃		200 ppb SO ₂ , 200 ppb O ₃ , NO ₂ ppb	25	80%	Copper
[39]	Vapor HNO ₃	7 days	325 µg/m ⁻³	25	65%	Copper
[40]	Mixture of SO ₂ , H ₂ S		SO ₂ 75, H ₂ S 50 (ppb)	25	75%	Copper
[41]	Mixture of SO ₂ , NO ₂	10, 30, 60 hour	SO ₂ 75, NO ₂ 120 (ppb)	25	75%	Copper
[42]	Formaldehyde, acetic and formic acid	135 days	0.04, 0.4, 4 ppmv	25	54%, 75%	Copper, lead
[43]	formic and acetic acid	21 days	100, 200, 300 ppm	30	100%	Copper
[44]	HNO ₃	2 weeks	126 (ppb)	25	65%	Copper,
[45]	NO ₂ , NO ₂ + SO ₂	2 weeks	800, 800 + 800 (µg/m ⁻³)	30	90%	Zinc
[46]	SO ₂	4 week	(10 ppm)	25	90%	Copper
[47]	SO ₂ + O ₃	4 week	476 ppb + 500 (ppb)	30	70%	Copper
[48]	NO ₂ + SO ₂	4 week	200 + 3000 (ppb)	25	90%	Steel
[49]	H ₂ S	4 week	50 - 200 (ppb)	25	80%	Copper
[50]	SO ₂ + NO ₂	14, 21, 28 days	200 and 800 (µg·m ⁻³)	35	70, 90	Copper
[29]	O ₃	24 h	500 ppb	25	50%, 90%	Silver

3. Results and Discussion

3.1. Examination of the Samples after the Test

All the coupons surfaces interacted with the gases from the first week except the exposed coupons to carbon dioxide. The reaction behavior inside the chamber and the growth rate of the tarnishing layer were similar among Cl, H₂S, and NO₂. The interaction began as a very thin layer on the surface and the growth of tarnishing was generally rapid then became slow. The surface appearance turned from light interference tones to a grey and, finally, black film. Also the tarnishing rate was increased with H₂S, Cl, decreased with SO₂, NO₂ as shown in **Figure 4**.

The Coupons were examined after each test by Visual examination, Polarizing Microscope and Scanning Electron Microscope to identify the morphology of the formed layer and evaluate the interaction between the coupons surface and the test gases. The investigation results revealed that the formed tarnishing layer, thickness, density and coverage of the surface were differed among the test coupons as shown in **Figure 5**. H₂S coupons recorded the highest thickness, density and coverage of the formed layer. Also H₂S caused pitting in the metallic core. Cl coupons were completely covered by a uniform general dense layer of silver tarnishing. CO₂ coupons revealed very weak effect of gas. Slightly tarnishing layer with green spots were observed on the surface of NO₂ coupons. SO₂ coupons showed the least tarnishing layer and the reaction was very slow although humidity existed, the slow reaction of SO₂ with silver was mention in previous studies [35].

3.2. The Analysis of Corrosion Products by X-Ray Diffraction and Raman Spectroscopy

The coupons were exposed to X-ray diffraction to analyze the formed patina.

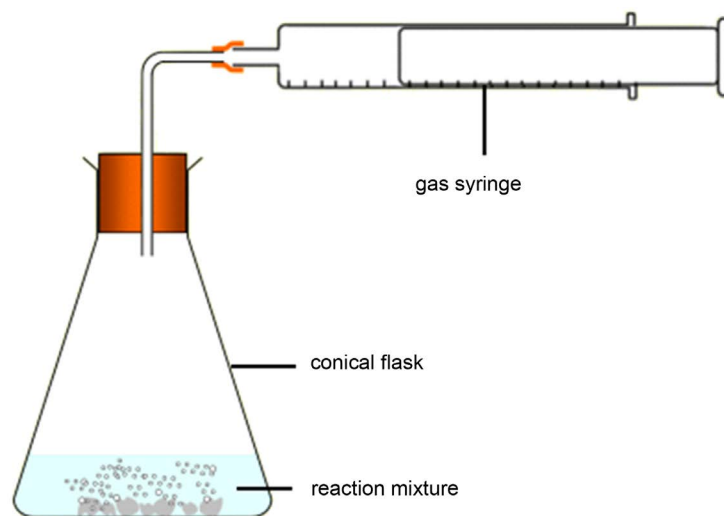


Figure 3. The syringe and the method of taking the required volume from the gas resulting from the interaction.

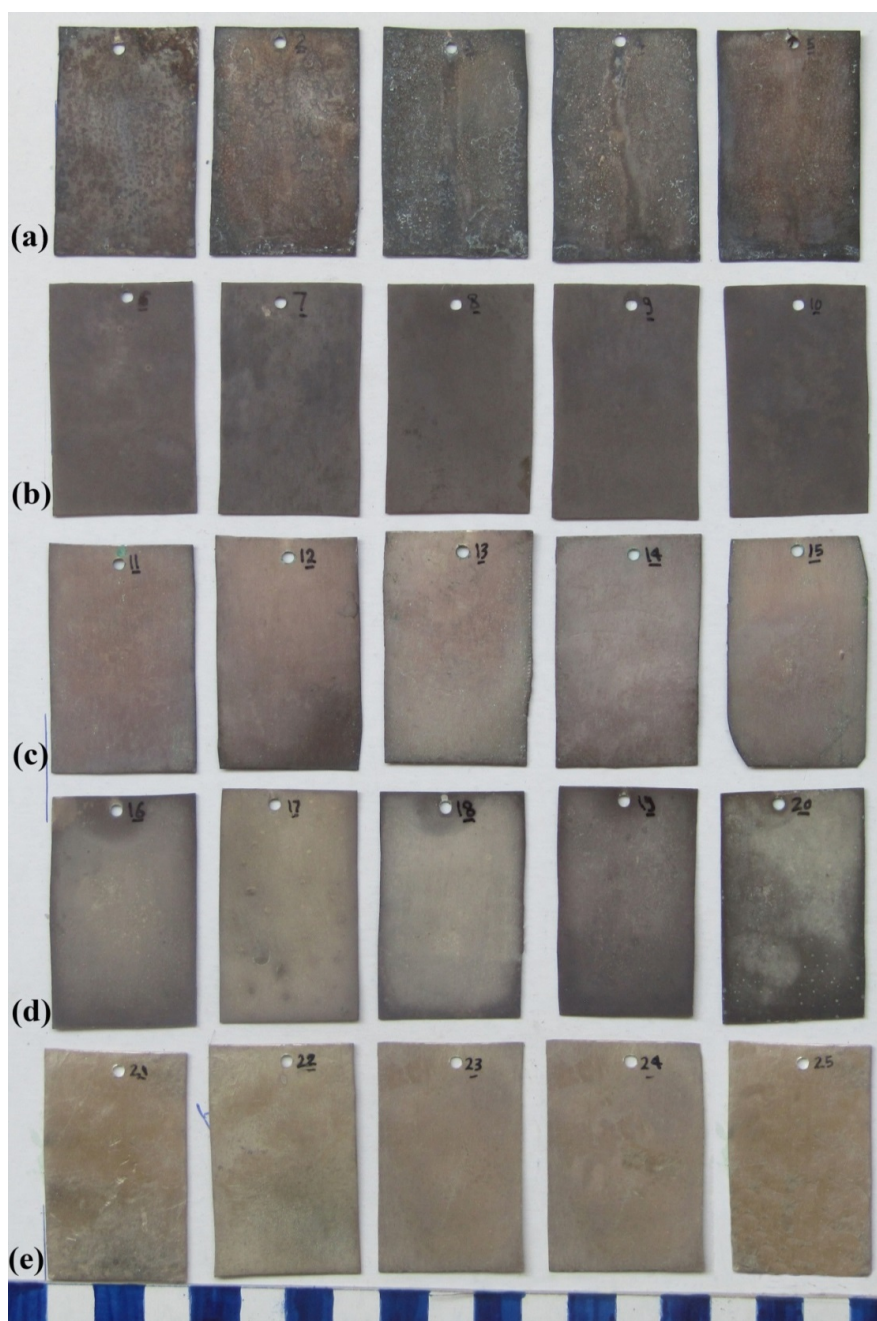


Figure 4. The coupons after the test: (a) The coupons exposed of H_2S ; (b) The coupons exposed of Cl; (c) The coupons exposed of SO_2 ; (d) The coupons exposed of NO_2 ; (e) The coupons exposed of CO_2 .

This was showed many of corrosion products as in **Figure 6** and **Table 3**.

The Raman spectrum of the tarnishing formed with H_2S shows four intensive bands in the range of $80 - 274 \text{ cm}^{-1}$, Apart from the bands related to silver lattice vibrations at 93 and 147 cm^{-1} , the others can be assigned to Ag-S-Ag symmetric stretching mode in particular at 93 , 188 and 243 cm^{-1} with a shoulder at 273 cm^{-1} [54]. The Raman spectrum confirmed XRD result because the bands revealed acanthite product **Figure 7(a)**.

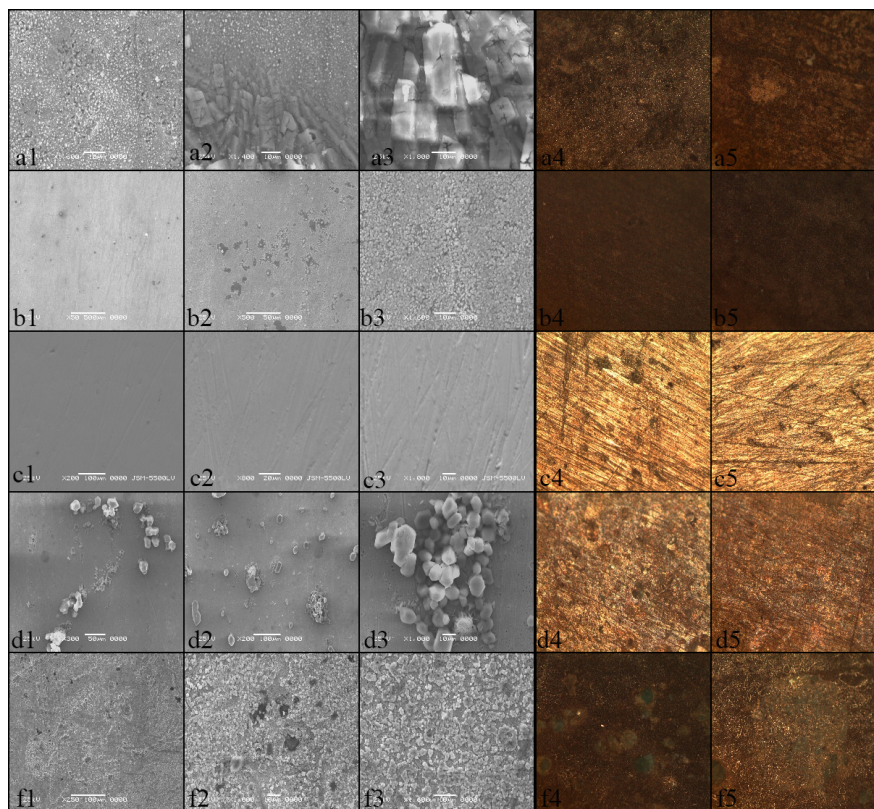


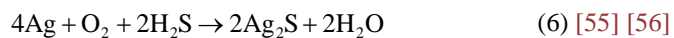
Figure 5. Investigation by SEM and polarizing microscope $\times 500$ show the most important characteristics of tarnishing layer on the surface such as H_2S coupons are covered by dense tarnishing layer (a1)-(a5); Cl coupons reveal a uniform and thick tarnishing layer (b1)-(b5); CO_2 coupons reveal very weak effect of the gas (c1)-(c5); SO_2 coupons reveal the crystal structure of product of tarnishing (d1)-(d5); Green spots on the surface of NO_2 coupons (f1)-(f5).

Table 3. Corrosion products on the coupons after the test.

SO2	Cl	CO ₂	H ₂ S	NO ₂
Ag	AgCl	Ag	Ag	Ag
Ag ₂ O	Ag ₂ O	AgO	Ag ₂ O	Ag ₂ O
Ag ₂ SO ₄	Ag	AgO	Ag ₂ S	Ag(NO ₃) ₃ (NO) ₃
			Ag ₂ CuS ₂	Cu ₂ (NO ₃)(OH) ₃

The Raman spectrum of Cl gas coupon presented sharp and highly intensive band at 236 cm^{-1} , two weak bands at 145 and 349 cm^{-1} , these beaks agreement with the main beaks of AgCl bands as in reference [54] **Figure 7(b)**, the layer tarnishing of other gases was so slight that it was not identified by Raman.

Silver sulfide (Ag₂S Acanthite): they were identified as abundant on silver artifacts. The reaction behavior between gas H₂S and the silver surface to form these products explains Equations (6) and (7).



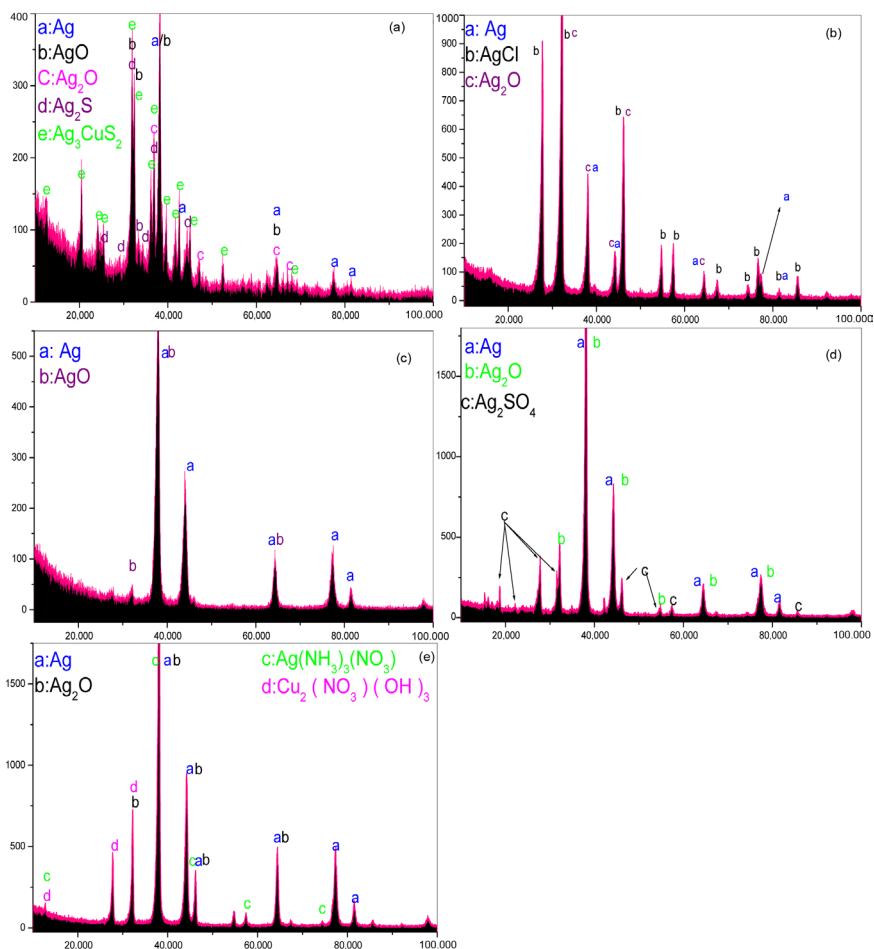
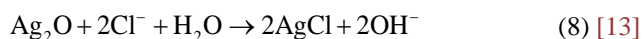
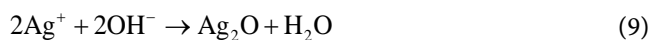


Figure 6. XRD patterns of tarnishing layers of the coupons: (a) Tarnishing of H_2S ; (b) Tarnishing of Cl ; (c) The coupons of CO_2 ; (d) Tarnishing of SO_2 ; (e) Tarnishing of NO_2 .

Silver chloride (AgCl Cerargyrite, chlorargyrite): In this case, the dominant theory in the interpretation of formation mechanism of chloroargyrite AgCl is the transformation of Ag_2O to AgCl as Equation (8) [13] [14]



Silver sulfite (Ag_2SO_4): This product was identified in a previous study as corrosion product of silver [1] and the Equations (9)-(12) were suggested for the mechanism of its formation on silver coupons surface.



Silver oxide Ag_2O : Silver artifacts react with oxygen either by the electrochemical reactions in the presence of humidity (Equations (13)-(15)) or by chemical reactions in the absence humidity (Equation (16)). Therefore Ag_2O and AgO are formed

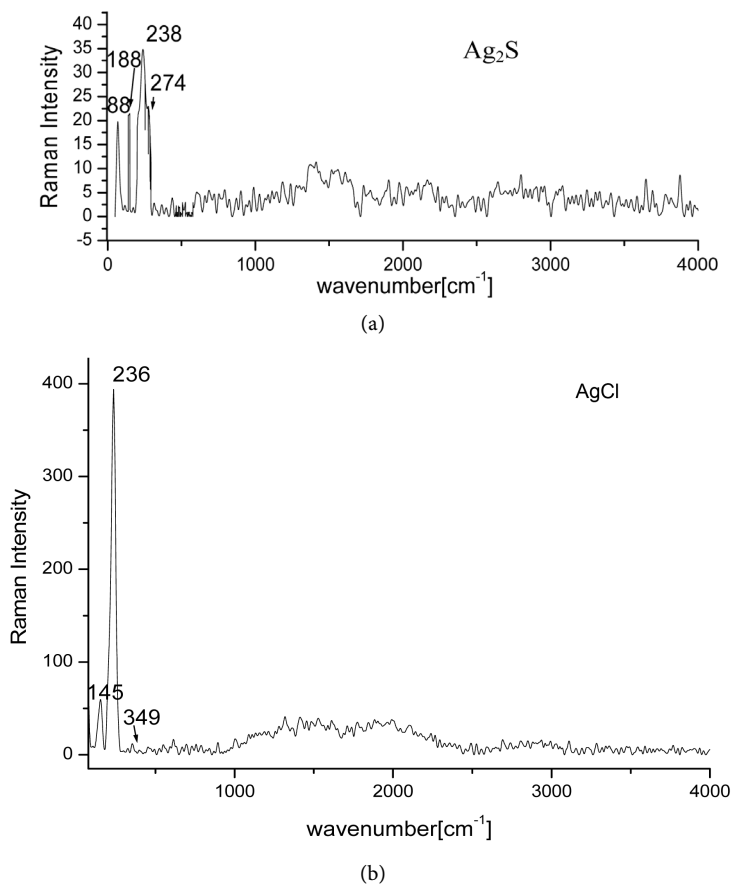
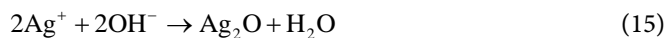


Figure 7. Raman spectrum of tarnishing of H₂S (a); tarnishing of Cl (b).

on silver artifacts surfaces.



Silver ammine nitrate ($\text{Ag}(\text{NO}_3)_3(\text{NO})_3$): previous studies of field and lab. exposure were identified only one product (AgNO_3) from nitrates anions as corrosion products on silver surface, Therefore this compound was expected of NO_2 gas, but analysis showed Silver ammine nitrate ($\text{Ag}(\text{NO}_3)_3(\text{NO})_3$).

Copper Nitrate Hydroxide (Rouaite, $\text{Cu}_2(\text{NO}_3)(\text{OH})_3$): Silver and copper are the coupons alloy elements, the formation of Rouaite corrosion product is contributed to selective corrosion of copper by the interaction of Cu (as the main alloying element) with NO_2 gas.

4. Conclusions

Silver in the ambient atmosphere and presence humidity is susceptible to the reac-

tion with air pollutants. The tarnishing is formed not only in the presence of Sulphur containing pollutants but also there are other gaseous such as Cl and NO₂.

Except the coupons of CO₂, all the test coupons were exposed to tarnishing layer which was formed on the surface as a blackish thin film caused by the reaction of the metal surface with test pollutants. But highest layer in density and tarnishing was to H₂S gas.

Found

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